

## DESCRIPTION

### HIGH TEMPERATURE BOLT MATERIAL

#### Technical Field

The present invention relates to a ferrite high temperature bolt material excellent in characteristics of resistance to stress relaxation at a high temperature, and more particularly to a heat treatment method for improving characteristics of resistance to stress relaxation, and a ferrite high temperature bolt material manufactured in this method.

#### Background Art

Bolt materials used in steam turbine plant for thermal power generation include 12Cr steel mainly used in a low temperature region (500°C or less) and Ni base superalloy used in a high temperature region. The 12Cr steel for a low temperature region is large in stress relaxation and it is hard to use in a high temperature region of 500°C or more, and Ni base superalloy is used in a high temperature region of over 500°C.

However, the turbine casing is manufactured of ferrite steel, coefficient of thermal expansion differs between casing and bolt, and design is complicated and difficult. If a ferrite high temperature bolt material usable at a high temperature is developed, it is not required to consider difference in coefficient of thermal expansion, and the steam turbine can be designed easily, and the structure can be simplified.

On the other hand, the Ni base superalloy is always expensive, and its manufacture or processing is not necessarily easy. Accordingly, steel materials usable in a high temperature region of 500°C or more are desired.

Indeed, price of ferrite steel is one-tenth of Ni base superalloy. If ferrite steel can be used as high temperature bolt material, the turbine design is easy and structure is simplified as discussed above. From the viewpoint of improvement of energy efficiency

of power generation, steam temperature tends to elevate every year, demand for bolt material usable at a high temperature is strong. Therefore, necessity of ferrite high temperature bolt material usable at a high temperature is extremely high, and its economical effects will be tremendous.

The inventors have specifically investigated into conventional bolt material of 12Cr steel, and evaluated the prior art as follows.

According to the standard of 12Cr high temperature bolt material (non-patent documents 1 and 2), as tempering condition, only the lowest temperature (593°C or 620°C) is specified. However, from the viewpoint of maintaining the strength characteristics such as proof stress, tempering is generally performed at a temperature of 700°C or less (non-patent document 3).

By contrast, materials for thermal power plant boilers are tempered at 730°C or higher, that is, higher than in bolt materials, in consideration of microstructure stability for long time. If tempered at a high temperature of 730°C or more, stress relaxation is large in a short time of about several hours, and the residual stress is smaller than in conventional 12Cr high temperature bolt material. However, since microstructure stability is high, in a long time exceeding hundreds of hours, degree of stress relaxation is decreased, and a higher residual stress than in conventional 12Cr high temperature bolt material is shown stably for a long time.

Improvements are attempted in Ni base superalloy, and, for example, a high temperature bolt material composed of Ni base superalloy comprising Cr 18 to 21 %, Ti 1.3 to 1.8 %, and Al 0.7 to 1.3 % has been proposed (patent document 1). But this is a superalloy, and is not intended to realize an inexpensive steel excellent in high temperature characteristics.

Non-patent document 1: ASTM A 193/A 193M-98a, Grade B6, B6X

Non-patent document 2: ASTM A 437/A 437M-99, Grade B4B, B4C

Non-patent document 3: H. Schaff, Performance of Bolting Materials in High

**Temperature Plant Applications, p. 410**

**Patent document 1: Japanese Patent Publication No. 3281685**

**The invention is devised in the light of the above background, and it is hence an object thereof to present a ferrite steel high temperature bolt material usable in a high temperature region of 500°C or more and excellent in characteristics of resistance to stress relaxation, and a method of manufacturing the same.**

#### **Disclosure of Invention**

**To solve the problems, it is a first aspect of the present invention to present a high temperature bolt material, being a ferrite steel having a tempered martensite structure comprising 8 wt % or more of Cr, and usable in a high temperature region of 500°C or more, and it is a second aspect to present a manufacturing method of high temperature bolt material characterized by quenching or normalizing a steel material containing Cr by 8 wt % or more at a temperature of 1000°C or more, and then tempering at a temperature of 730°C or more.**

**Since the high temperature bolt material of the invention is a bolt material usable in a high temperature region of 500°C or more, it is called "high temperature bolt material."**

**The invention, as bolt material not predicted or estimated from the prior art, presents a ferrite steel high temperature bolt material excellent in characteristics of resistance to stress relaxation and usable in a high temperature region of 500°C or more, and a method of manufacturing the same.**

**The existing ferrite high temperature bolt material is low in characteristics of resistance to stress relaxation at a high temperature, and cannot be used at a high temperature of 500°C or more, and hence at a high temperature of 500°C or more, Ni base superalloy high in high temperature strength has been used. However, since the turbine casing is manufactured of ferrite steel, coefficient of thermal expansion differs between**

casing and bolt, and the design is complicated and difficult. By this invention, ferrite high temperature bolt material usable at a high temperature is realized, and difference in coefficient of thermal expansion is not taken into consideration, and the design of steam turbine becomes easy, and the structure is simplified.

Being a ferrite steel, the high temperature bolt material of the invention is presented at a cost of 1/10 or less of Ni base superalloy conventionally used as high temperature bolt material.

#### **Brief Description of Drawings**

Fig. 1 is a microscopic image of microstructure of steel of the present invention.

Fig. 2 shows characteristics of resistance to stress relaxation of high temperature bolt material of the invention and a comparative material.

#### **Best Mode for Carrying Out the Invention**

The present invention has features as described above, and one of its embodiments is explained below.

The high temperature bolt material of the invention is a ferrite steel comprising 8 wt % or more of Cr (chromium) in chemical composition, and having a tempered martensite structure as microstructure. A more preferred chemical composition includes the following components.

**C:** It forms carbide or carbonitride and effective to add by 0.04 wt % or more for improving strength, but if added by more than 0.2 wt %, strength is lowered in a long time range.

**Si:** an important element for assuring resistance to oxidation, and 0.01 wt % or more is preferred, but if exceeding 0.9 wt %, toughness is lowered, and creep rupture strength is lowered.

**Mn:** an element functioning as deoxidation agent, added preferably in the range

of 0.3 to 1.5 wt %.

**Cr:** 8.0 wt % or more is needed for assuring resistance to oxidation, but if exceeding 13.5 wt %, delta ferrite phase is generated, and strength is lowered.

**Mo:** effective for solid solution strengthening, but if exceeding 2.0 wt %, brittleness is promoted.

**W:** effective for solid solution strengthening, but if exceeding 4.0 wt %, brittleness is promoted.

**V:** effective by 0.02 wt % or more for forming carbonitride and enhancing strength, but if exceeding 0.35 wt %, undissolved precipitates increase and it is not effective for strength.

**Nb:** effective by 0.01 wt % or more for forming carbonitride and enhancing strength, but if exceeding 0.2 wt %, undissolved precipitates increase and it is not effective for strength.

**Co:** effective for assuring high temperature strength because generation of delta ferrite phase is suppressed, but if exceeding 4.0 wt %, long time strength is lowered.

**Ni:** effective for assuring high temperature strength because generation of delta ferrite phase is suppressed, but not effective if exceeding 3.0 wt % because transformation temperatures of ferrite and austenite are lowered.

**Al:** important as deoxidation agent, preferably contained by 0.01 wt % or less.

**N:** 0.002 wt % or more is effective for forming carbide or carbonitride and improving strength, but if exceeding 0.15 wt %, manufacturing is difficult.

**B:** effective for improving strength at about 0.02 wt % or less because precipitates are refined and stability at a high temperature is improved.

In the manufacturing method of the invention, the following points are important.

A quenching or normalizing temperature is 1000°C or more, and a tempering temperature is 730°C or more. That is, in quenching or normalizing, a temperature must

be kept at 1000°C or more in order to form austenite single phase and form a solid solution of alloying elements such as V and Nb in base phase.

In tempering, to enhance high temperature stability of tempered martensite structure, tempering heat treatment at 730°C or more is needed. A general tempering temperature of conventional ferrite high temperature bolt material is 700°C or lower (see non-patent document 3), and in a thermal power plant boiler required to have enough high temperature stability of microstructure, a general tempering temperature of high Cr ferrite heat resistant steel is specified to be 730°C or more (Thermal Power Plant Standard, Japan Society of Mechanical Engineers, 2002).

An example is shown below, and the invention is more specifically described. It must be noted, however, that the invention is not limited to this example alone.

#### **Example**

Sample materials were manufactured in a chemical composition as shown in Table 1. The sample materials were heat treated in the condition specified in Table 2. Tempering temperature of comparative material is 640°C, and a tempering temperature of the steel of the invention is 800°C, and it is a feature of the high temperature bolt material of the invention that it is tempered at a higher temperature than in the comparative material. Fig. 1 is a microscopic image of microstructure of the steel of the invention. Grain size of martensite phase is about 50  $\mu\text{m}$ .

**Table 1**

| Sample material        | C     | Si   | Mn   | P     | S     | Ni   | Cr    | Mo   | W    |
|------------------------|-------|------|------|-------|-------|------|-------|------|------|
| Steel of the invention | 0.077 | 0.29 | 0.50 | 0.002 | 0.002 | —    | 9.28  | —    | 3.13 |
| Comparative material   | 0.21  | 0.44 | 0.62 | 0.023 | 0.004 | 0.85 | 11.46 | 0.97 | 0.94 |

  

| Sample material        | Co   | V    | Nb    | Ti    | Sn    | Al    | N      | B      | Fe      |
|------------------------|------|------|-------|-------|-------|-------|--------|--------|---------|
| Steel of the invention | 3.03 | 0.20 | 0.045 | —     | —     | 0.002 | 0.0024 | 0.0130 | balance |
| Comparative material   | 0.10 | 0.28 | —     | 0.090 | 0.027 | 0.033 | 0.0239 | —      | balance |

**Table 2**

| Sample material        | Heat treatment condition     |                             |
|------------------------|------------------------------|-----------------------------|
|                        | Quenching/normalizing        | Tempering                   |
| Steel of the invention | 1080°C/60 min. → air cooling | 800°C/60 min. → air cooling |
| Comparative material   | 1050°C/25 min. → oil cooling | 640°C/60 min. → air cooling |

Stress relaxation behavior of sample material at 650°C is shown in Fig. 2. Right after start of test, the residual stress of the steel of the invention is smaller than that of comparative material. However, as the holding time exceeds about 100 hours, degree of drop of residual stress is decreased in the steel of the invention, and a nearly constant value of about 40 MPa is shown. In the comparative material, by contrast, for tens of hours after start of test, the residual stress is higher than the steel of the invention, but as the holding time exceeds 100 hours, the residual stress is lowered substantially. In the long time range of holding time exceeding 100 hours, the steel of the invention shows a higher residual stress than the comparative material, and it is known that the steel of the invention is superior in characteristics of resistance to stress relaxation. It is a great feature of high temperature bolt material of steel of the invention that resistance to stress relaxation is excellent in long time range of over 100 hours.

#### **Industrial Applicability**

By the high temperature bolt material of the invention, an inexpensive ferrite bolt material excellent in high temperature characteristics is presented.

Indeed, the price of ferrite steel is less than 1/10 of Ni base superalloy. By using ferrite steel, for example, in high temperature bolt material, the turbine design becomes easy, and the structure is simplified. From the viewpoint of improvement of energy efficiency in power generation, steam temperature tends to rise every year, and there is an increasing demand for bolt material usable at a high temperature. Therefore, ferrite high temperature bolt material usable at a high temperature is very much demanded, and its economical effect is tremendous.